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Ecosystem-level Evaluation of Intrinsic Contaminant Bioremediation and Impact of Naval Shipyards on Adjacent Ecosystems: A Preliminary Report

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Landover, Maryland

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Chemistry Division

February 27, 1998

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A phase I evaluation of intrinsic contaminant bioremediation was conducted 21-23 July 1997 at a former Defense Reutilization and Marketing Office (DRMO) site at the Charleston Naval Shipyard, Charleston, SC. The objective of the project is to determine the extent to which intrinsic bioremediation is occurring in groundwater contaminated with gasoline (benzene, ethylbenzene, toluene, and xylenes; BTEX), methyl-tertbutyl ether (MTBE), and trichloroethylene (TCE). Preliminary findings suggest that the comingled contaminant plumes have significant bacterial productivity and contaminant mineralization rates. Rapid bacterial production and benezene turnover rates at wells, which are down gradient of the other BTEX plume(s) suggests that the natural bacterial assemblage has the capacity to inhibit migration of the plume towards Noisette Creek. Low ratios of DCE:TCE were found near the expected source but greatly increased as the plume moved towards creek suggesting that *in situ* biodegradation is occurring. Benzene concentrations did not correlate with changes in bacterial production in the TCE-impacted wells though even in low concentrations. Data suggest there may be three separate BTEX plumes, two from unleaded gasoline, and one from leaded gasoline.

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Ecosystem-Level Evaluation of Intrinsic Contaminant Bioremediation and Impact of Naval Shipyards on Adjacent Ecosystem: A Preliminary Report

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U.S. Naval Research Laboratory

Abstract

A phase I evaluation of intrinsic contaminant bioremediation was conducted 21-23 July 1997 at a former Defense Reutilization and Marketing Office (DRMO) site at the Charleston Naval Shipyard, Charleston, SC. The objective of the project is to determine the extent to which intrinsic bioremediation is occurring in groundwater contaminated with gasoline (benzene, ethylbenzene, toluene, and xylenes; BTEX), methyl-tertbutyl ether (MTBE), and trichloroethylene (TCE). Preliminary findings suggest that the comingled contaminant plumes have significant bacterial productivity and contaminant mineralization rates. Rapid bacterial production and benzene turnover rates at wells, which are down gradient of the other BTEX plume(s) suggests that the natural bacterial assemblage has the capacity to inhibit migration of the plume towards Noisette Creek. Low ratios of DCE:TCE were found near the expected source but greatly increased as the plume moved towards creek suggesting that *in situ* biodegradation is occurring. Benzene concentrations did not correlate with changes in bacterial production in the TCE-impacted wells though even in low concentrations. Data suggest there may be three separate BTEX plumes, two from unleaded gasoline, and one from leaded gasoline.

Manuscript approved January 20, 1998

Executive Summary

BTEX

- Highest concentrations of BTEX observed at NBCA-039-11
- Bacterial degradation (utilization) of benzene and toluene highest at BTEX plume (NBCA-039-001)
- High benzene turn-over rates and high utilization rates suggest that the plume is rapidly being mineralized by heterotrophic bacteria.
- Low bacterial production (metabolism) coupled with other data suggest that BTEX is the major carbon source
- Rapid bacterial production and benzene turnover rates at wells NBCA-039-009 and -010, which are down gradient of the other BTEX plume(s) suggests that the natural bacterial assemblage has the capacity to inhibit migration of the plume towards Noisette Creek

TCE

- The source of the TCE appears to be near wells NBCA-039-012 and 039-003
- Low ratios of DCE:TCE (Table 1) were found near the expected source but greatly increased as the plume moved towards creek (NBCA039-009, 013) suggesting that *in situ* biodegradation is occurring
- Benzene concentrations did not correlate with changes in bacterial production in the TCE-impacted wells though even in low concentrations
- Low concentrations of TCE correlated with a reduction in heterotrophic activity down to a baseline level

MTBE

- Data suggest there may be three separate BTEX plumes, two from unleaded gasoline (NBCA-039-1 and 039-04), and one from leaded gasoline (NBCA-039-11)
- MTBE is associated with the TCE plume (NBCA-039-012).
- MTBE concentration had no correlation with BTEX concentration
- A strong correlation exists between TCE and MTBE concentration

List of Figures

BTEX

Figure 12. In BTEX impacted wells, production ($\mu g\ C\ L^{-1}\ h^{-1}$) increased with increasing benzene concentration ($\mu g\ L^{-1}$).
Benzene caused bacterial production to decrease in relatively uncontaminated wells (Fig. 10), but production increases rapidly in the highly BTEX-contaminated wells with benzene (Fig. 11) or total BTEX concentration (Fig. 12)[1]. This suggests that as the BTEX plume migrates into an area that is unimpacted by TCE or BTEX, there could be an initial decrease in bacterial metabolism and thus total productivity. In this instance, benzene may either be inhibitory to the natural assemblage or may be less efficiently metabolized as an energy source.

Figure 13. In relatively unimpacted wells, there was little relationship between production ($\mu g\ C\ L^{-1}\ h^{-1}$) and BTEX concentration ($\mu g\ L^{-1}$).

Figure 14. In TCE impacted wells, production ($\mu g\ C\ L^{-1}\ h^{-1}$) generally decreased with increasing BTEX concentration ($\mu g\ L^{-1}$).

Figure 15. In BTEX impacted wells, benzene utilization ($\mu g\ C\ L^{-1}\ h^{-1}$) decreased with increasing bacterial production ($\mu g\ C\ L^{-1}\ h^{-1}$). In wells with high BTEX contamination, benzene mineralization (utilization) is inversely correlated with bacterial production suggesting that benzene is being inefficiently utilized (rather than inhibitory).

TCE

Figure 16. TCE concentration (relative abundance) is elevated in MW-12 with lower concentration down gradient.

Figure 17. DCE concentration (relative abundance) is elevated in MW-12 with lower concentration down gradient.

Figure 18. Toluene turnover times (h^{-1}) were very rapid in the TCE plume.
Low ratios of DCE:TCE (Table 1) were found near the expected source but greatly increased as the plume moved towards creek (NBCA039-009, 013). This evidence coupled with the high toluene turnover rates in the plume (Fig. 18) suggests that the TCE is being degraded by the natural bacterial assemblage. The impact on the creek is difficult to determine without measuring TCE mineralization and groundwater transport rates and possibly having monitoring wells closer to the creek.

Figure 19. In TCE impacted wells, production ($\mu g\ C\ L^{-1}\ h^{-1}$) had little relationship with benzene concentration ($\mu g\ L^{-1}$). Unlike in the both unimpacted and BTEX-impacted areas, benzene concentrations did not correlate with changes in bacterial production in the

[1] There was not a clear relationship between total BTEX and production at the unimpacted (Fig. 13) and TCE-impacted wells (Fig. 14).

TCE-impacted wells though even in low concentrations, TCE inhibited bacterial production down to a baseline.

Figure 20. In TCE impacted wells, production ($\mu g\ C\ L^{-1}\ h^{-1}$) decreased with TCE concentration (relative abundance). In the TCE-impacted wells, even low concentrations of TCE correlated with a reduction in heterotrophic activity down to a baseline level ($1.2 \times 10^{-1}\ \mu g\ C\ L^{-1}\ h^{-1}$)

Figure 21. In TCE impacted wells, toluene utilization ($\mu g\ C\ L^{-1}\ h^{-1}$) increased with increasing bacterial production ($\mu g\ C\ L^{-1}\ h^{-1}$). Though it is possible that TCE inhibits bacterial metabolism of some component of the natural assemblage, it is more likely that the decreased production is a result of reduced metabolic efficiency of toluene degradation. In these wells, heterotrophic production correlated well with toluene utilization. TCE is cometabolized along with toluene metabolism though it is not used as an energy source. This would reduce metabolic efficiency of the natural assemblage and contribute to lower production in the presence of TCE.

MTBE

Figure 22. MTBE concentration ($\mu g\ L^{-1}$) is elevated in MW-1, -12, & -14 suggesting at least two sources are present.

Figure 23. In BTEX impacted wells, BTEX concentration ($\mu g\ L^{-1}$) had little relationship with MTBE concentration ($\mu g\ L^{-1}$). MTBE is associated with the TCE plume (NBCA-039-012). MTBE concentration had no correlation with BTEX concentration suggesting that at least one source of the BTEX was not from unleaded fuel (NBCA-039-011).

Figure 24. In TCE impacted wells, TCE concentration ($\mu g\ L^{-1}$) positively correlated with MTBE concentration ($\mu g\ L^{-1}$). Surprisingly, there was a strong correlation between TCE and MTBE concentration suggesting that they are co-contaminants with a common source that are being diluted by groundwater transport.

Figure 25. In relatively unimpacted wells, there was some correlation between MTBE concentration ($\mu g\ L^{-1}$) and bacterial production ($\mu g\ C\ L^{-1}\ h^{-1}$).

Figure 26. When combining data from all wells, there was little correlation between MTBE concentration ($\mu g\ L^{-1}$) and bacterial production ($\mu g\ C\ L^{-1}\ h^{-1}$).
There was some increase in bacterial production with MTBE concentration in the relatively unimpacted wells (Fig. 25) though this was not seen when all well data was included (Fig. 26).

List of Tables

Table 1. Contaminant concentrations and biological analyses from July 21-23, 1997 sampling of CNY DRMO site.

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Phase I DRMO Site 21-23 July 1997

Total BTEX concn. ($\mu g\ l^{-1}$) profiles are heavily influenced by MW-11 values.

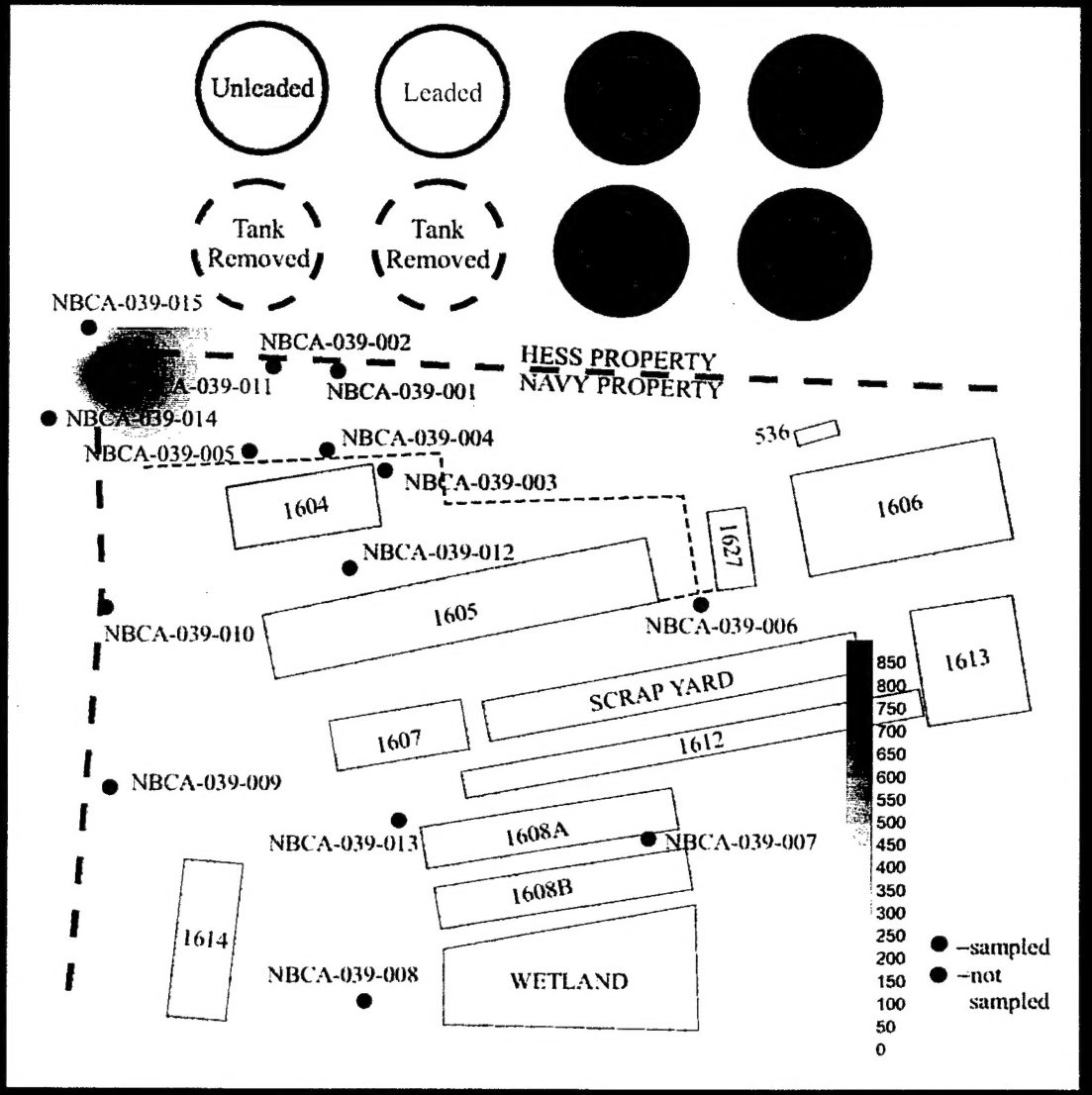

Figure 1.

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Ethylbenzene concn. ($\mu g\ l^{-1}$) is elevated in MW-11 but in MW-1 in contrast with benzene concn.

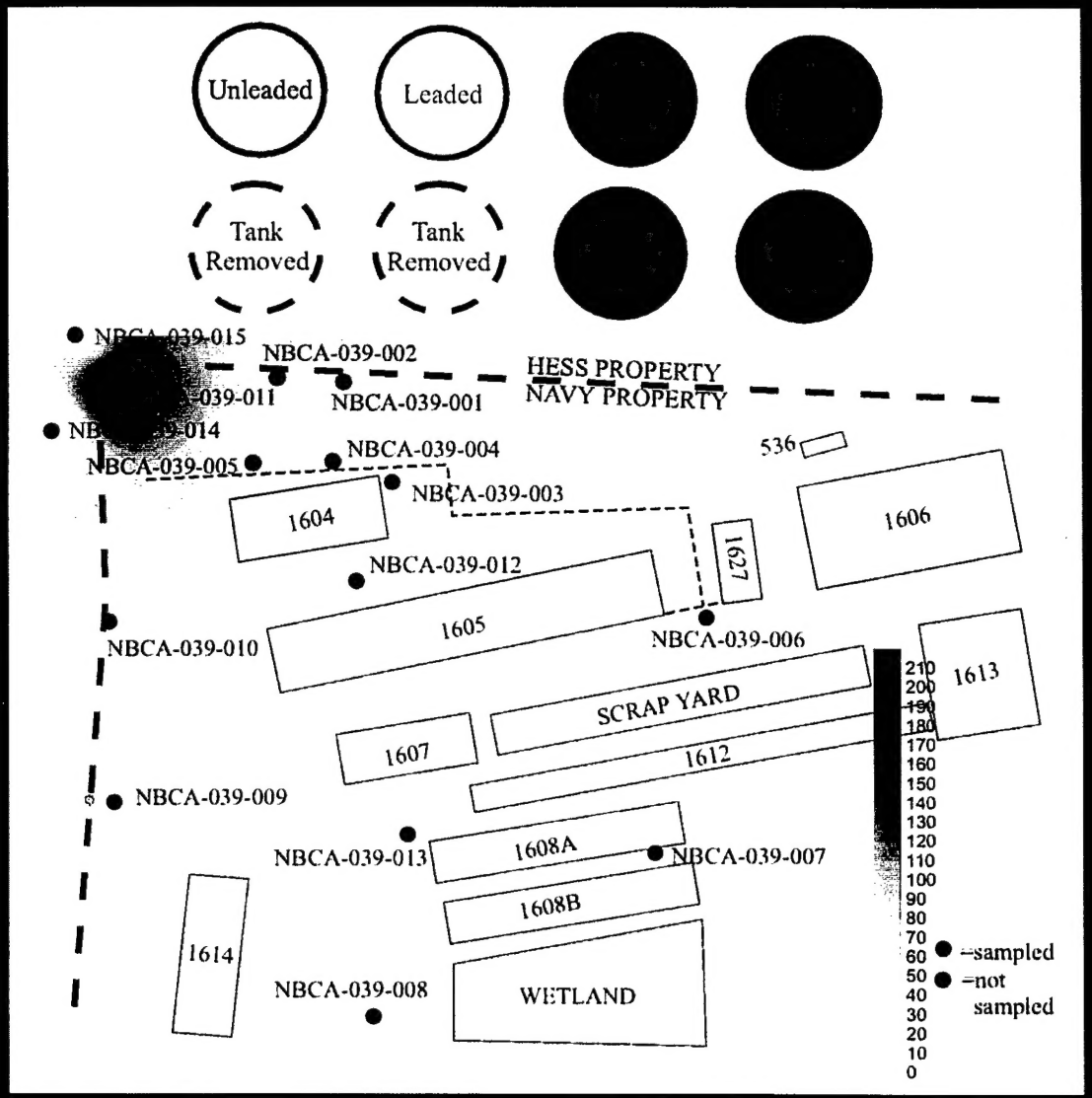

Figure 2.

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Phase I DRMO Site 21-23 July 1997

p-Xylene concn. ($\mu g\ l^{-1}$) is elevated in MW-11 as was concn. of ethylbenzene.

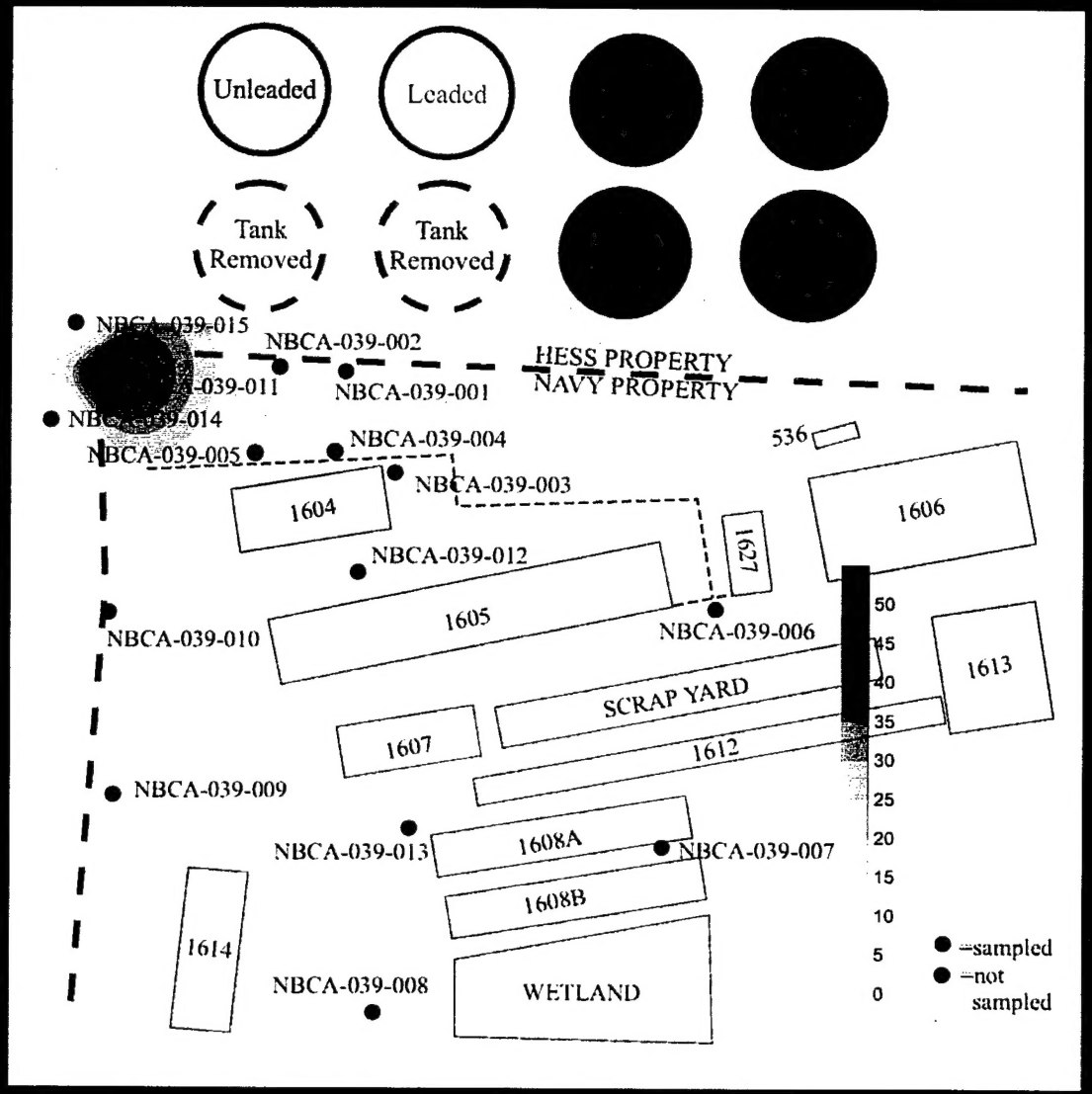

Figure 3.

Figure 4.

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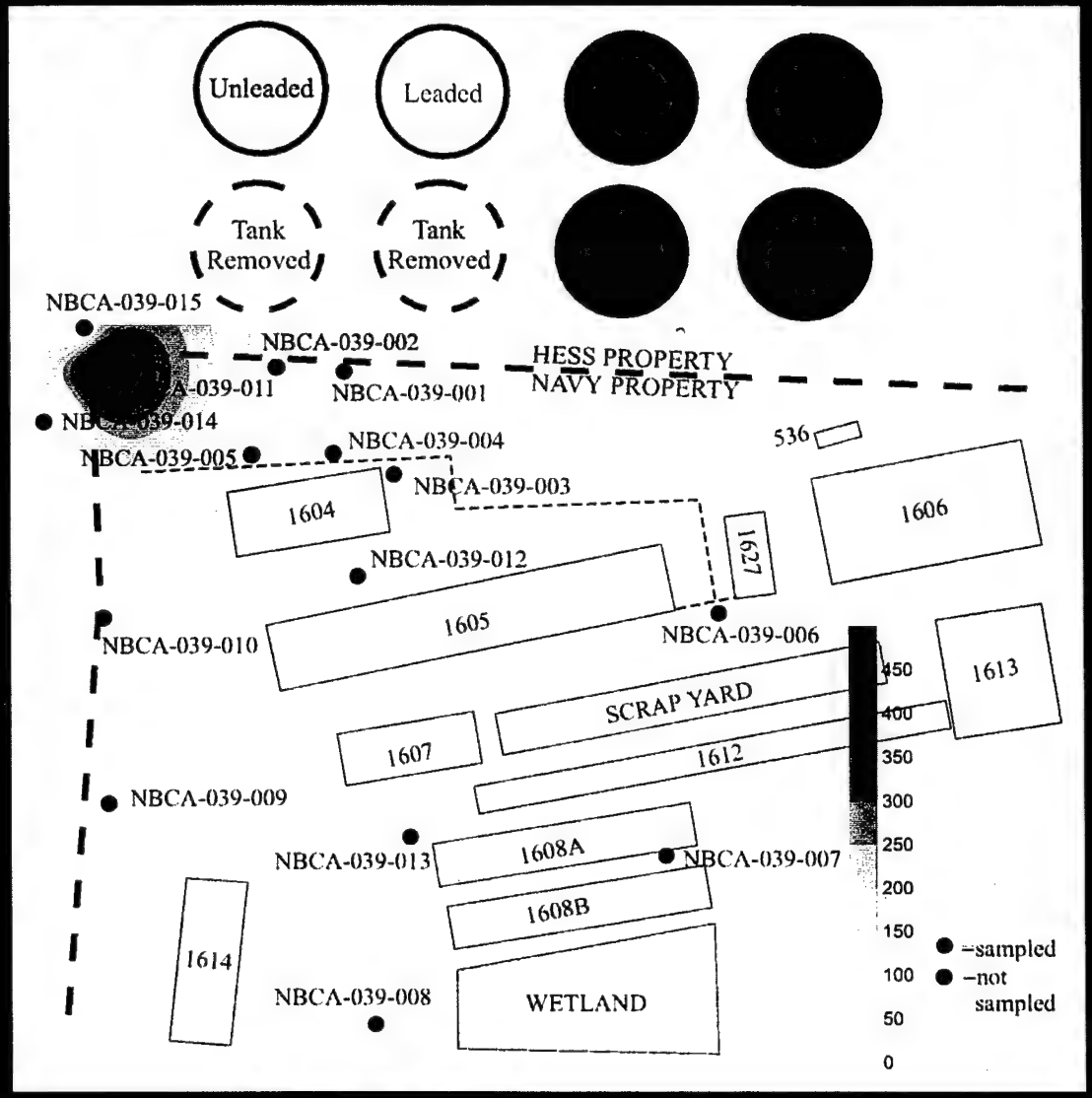
Phase I DRMO Site 21-23 July 1997

o-, *m*-Xylenes concn. ($\mu g\ l^{-1}$) is elevated in MW-11 as was concn. of ethylbenzene



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Benzene concn. ($\mu g\ l^{-1}$) is elevated in MW-11 & -1 but rapidly decreases with distance. Plumes may not be distinct as MW-2, -5 were not sampled.

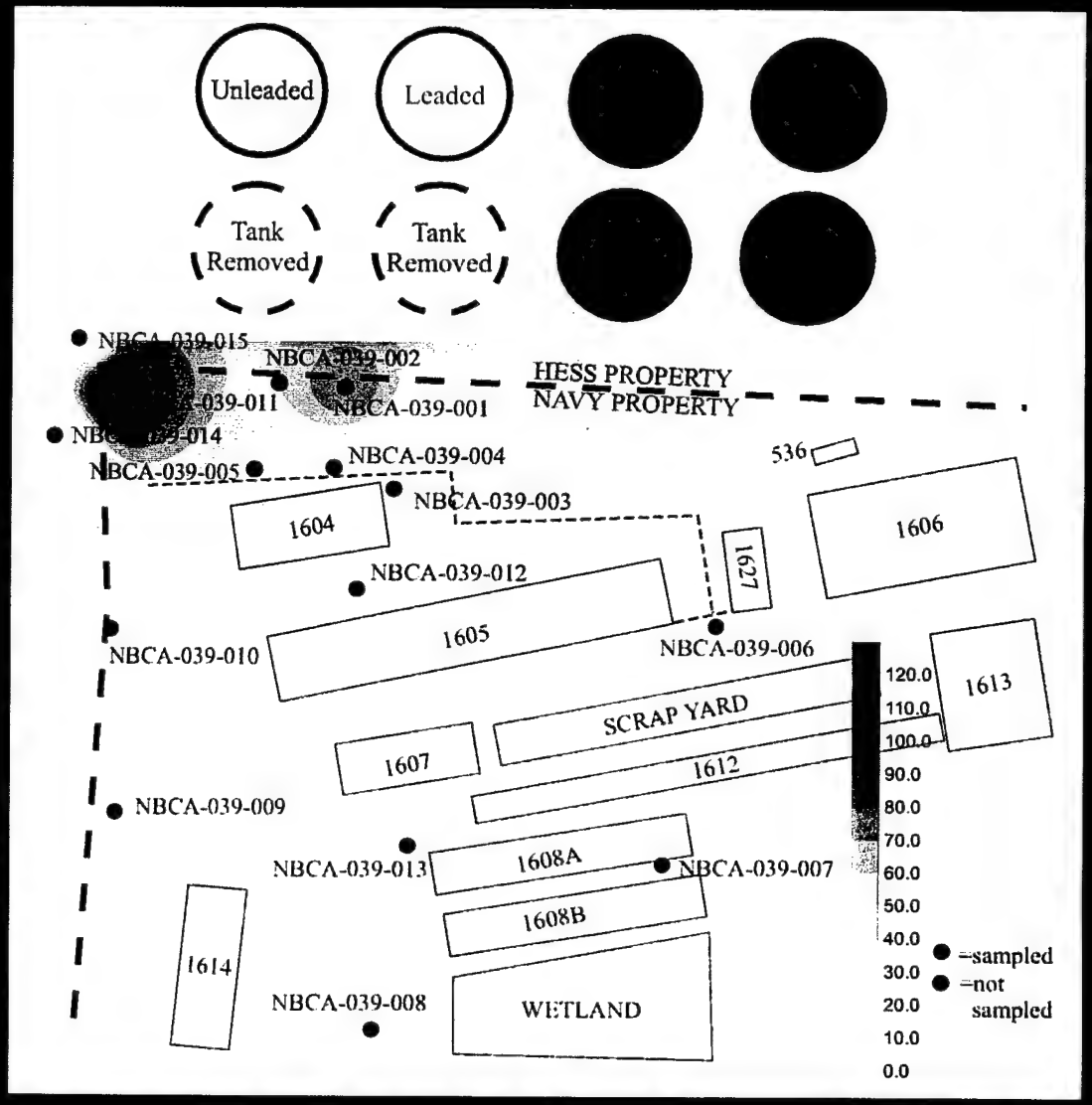

Figure 5.

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Phase I DRMO Site 21-23 July 1997

Benzene utilization ($\mu g\ l^{-1}\ h^{-1}$) is highest at MW-1.

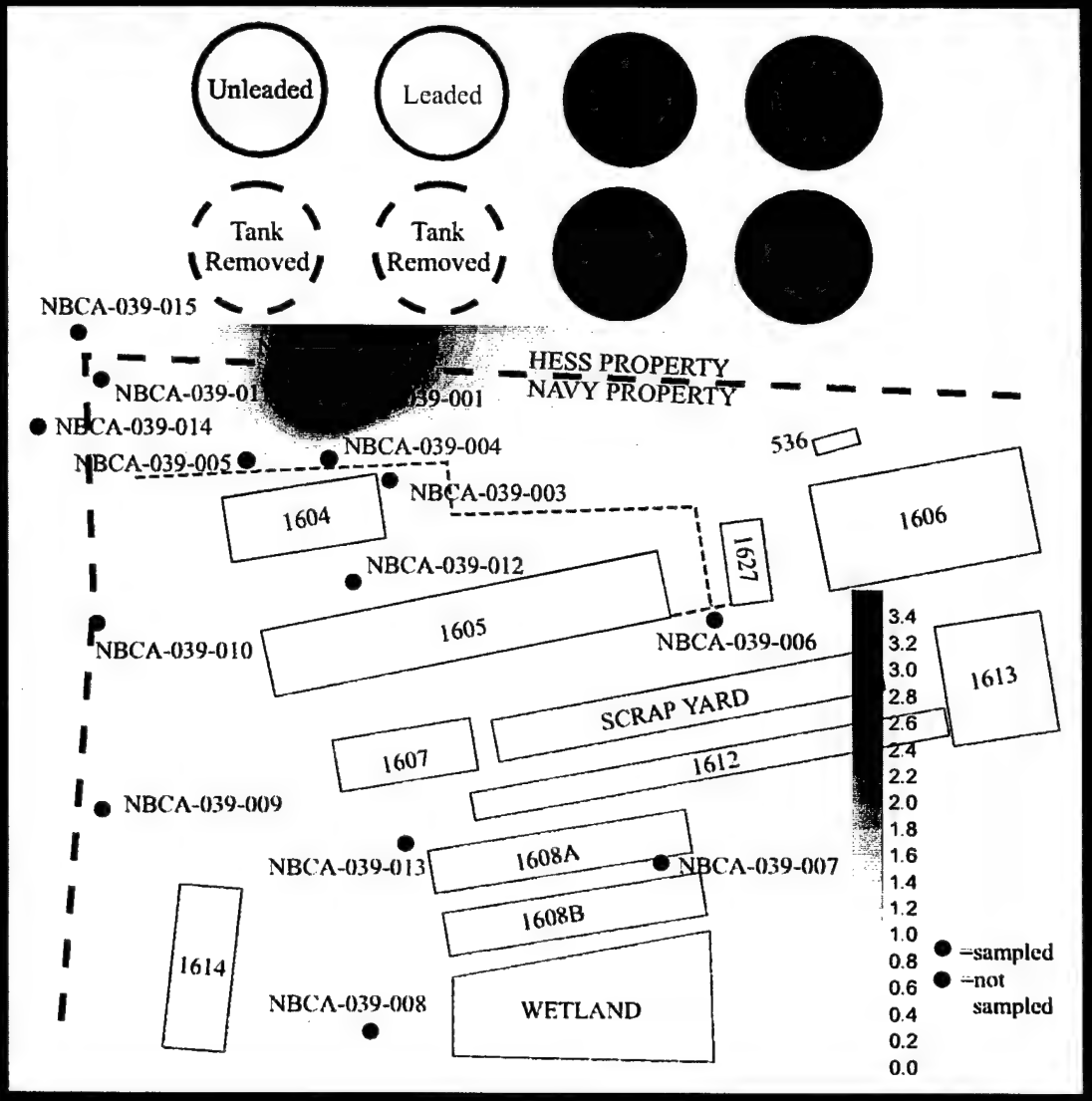

Figure 6.

Figure 7.

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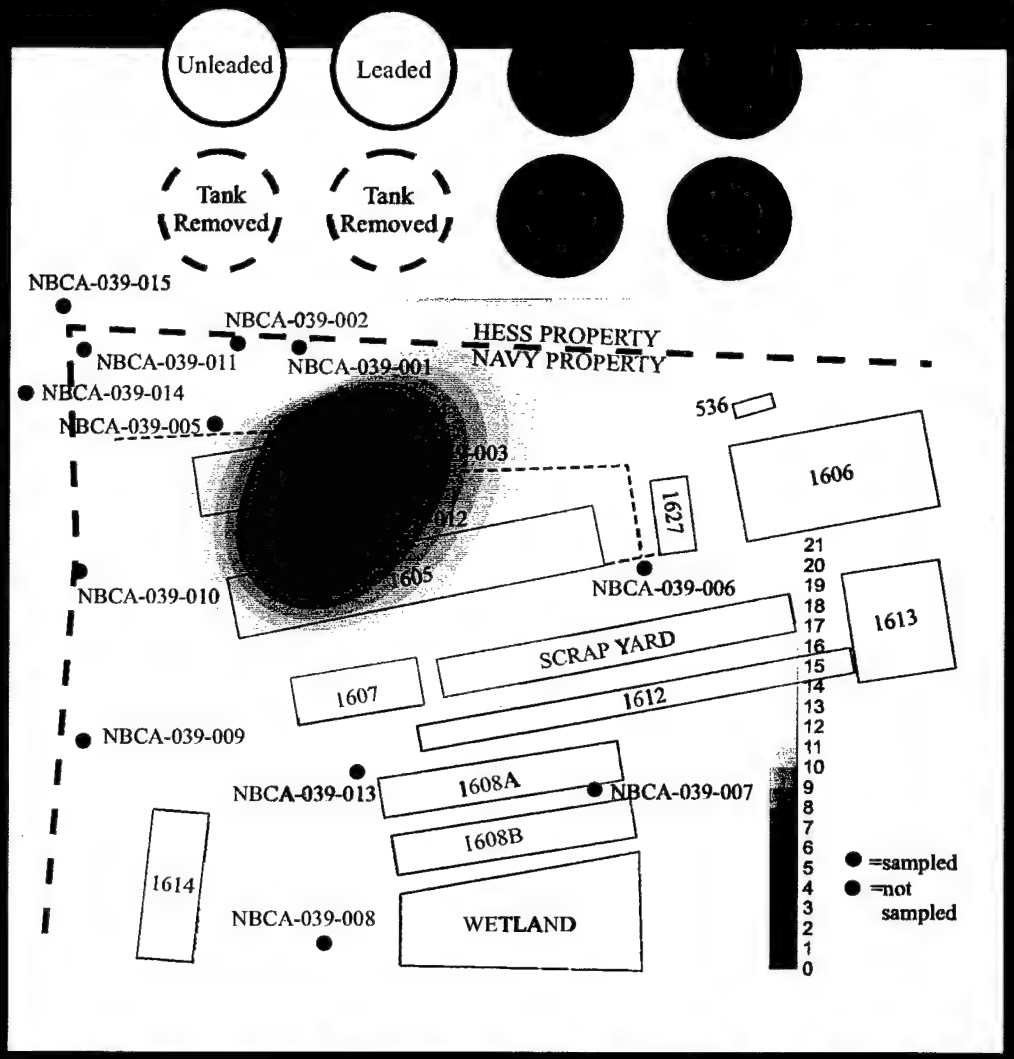
Phase I DRMO Site 21-23 July 1997

Toluene turnover times (h^{-1}) were very rapid in the TCE plume.



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Benzene turnover times (h^{-1}) were rapid downgradient of the BTEX spill and in the TCE plume as well as at MW-7.

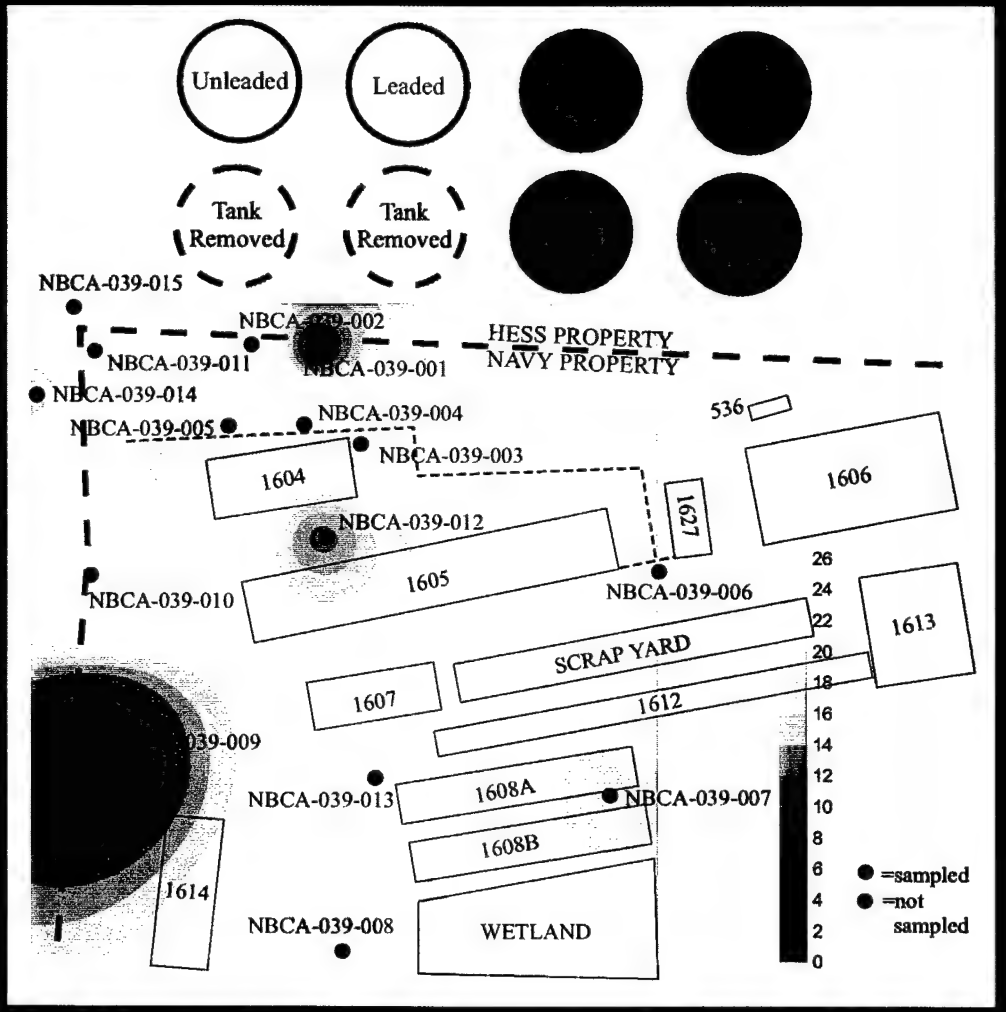

Figure 8.

Figure 9.

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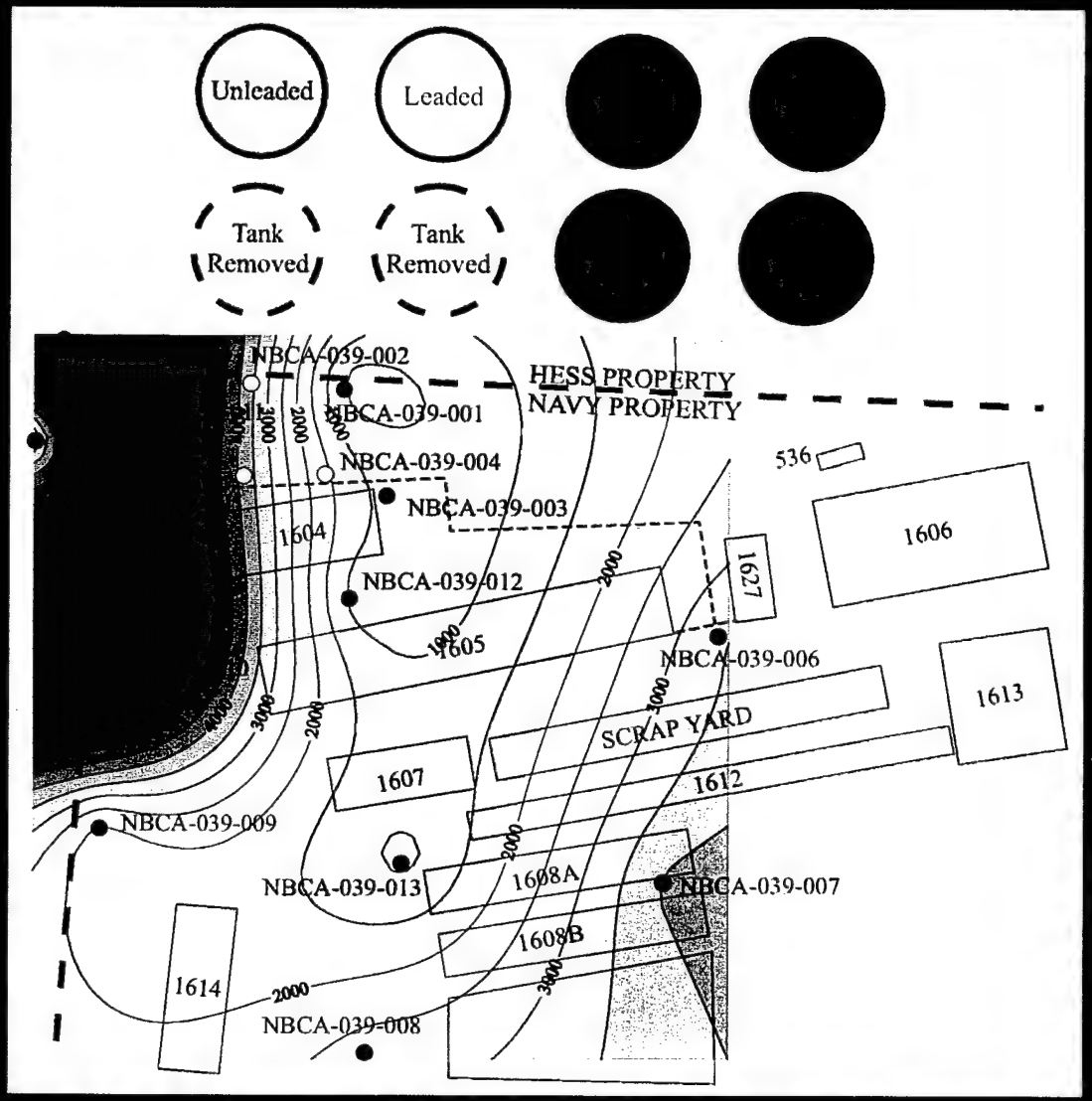
Bacterial production (cells ml^{-1} h^{-1}) in groundwater samples was elevated in the BTEX plume near the Hess border, as well as near a plume by buildings 1608A and 1608B.



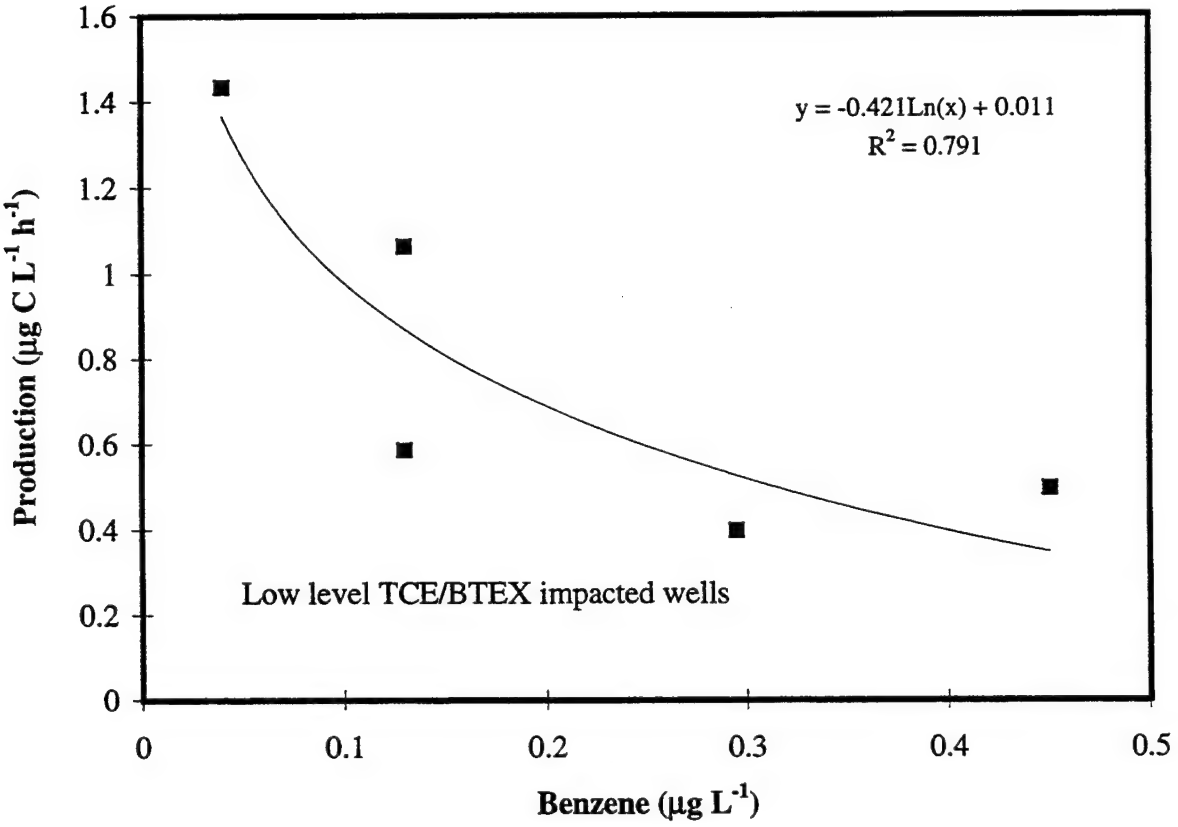

y = -0.421Ln(x) + 0.011
R^2 = 0.791
Low level TCE/BTEX impacted wells
Production (µg C L^{-1} h^{-1})
Benzene (µg L^{-1})
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
0.1
0.2
0.3
0.4
0.5

Figure 10.

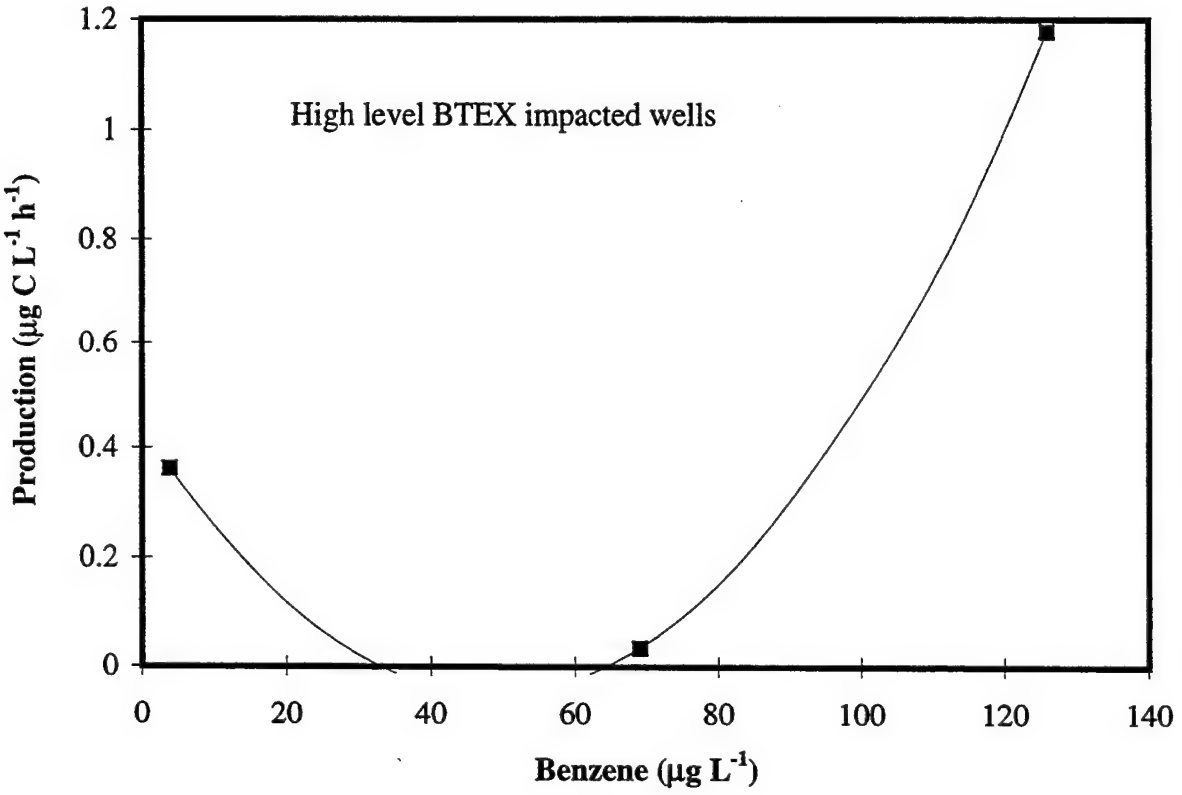

High level BTEX impacted wells
Production (µg C L-1 h-1)
Benzene (µg L-1)
1.2
1
0.8
0.6
0.4
0.2
0
0
20
40
60
80
100
120
140

Figure 11.

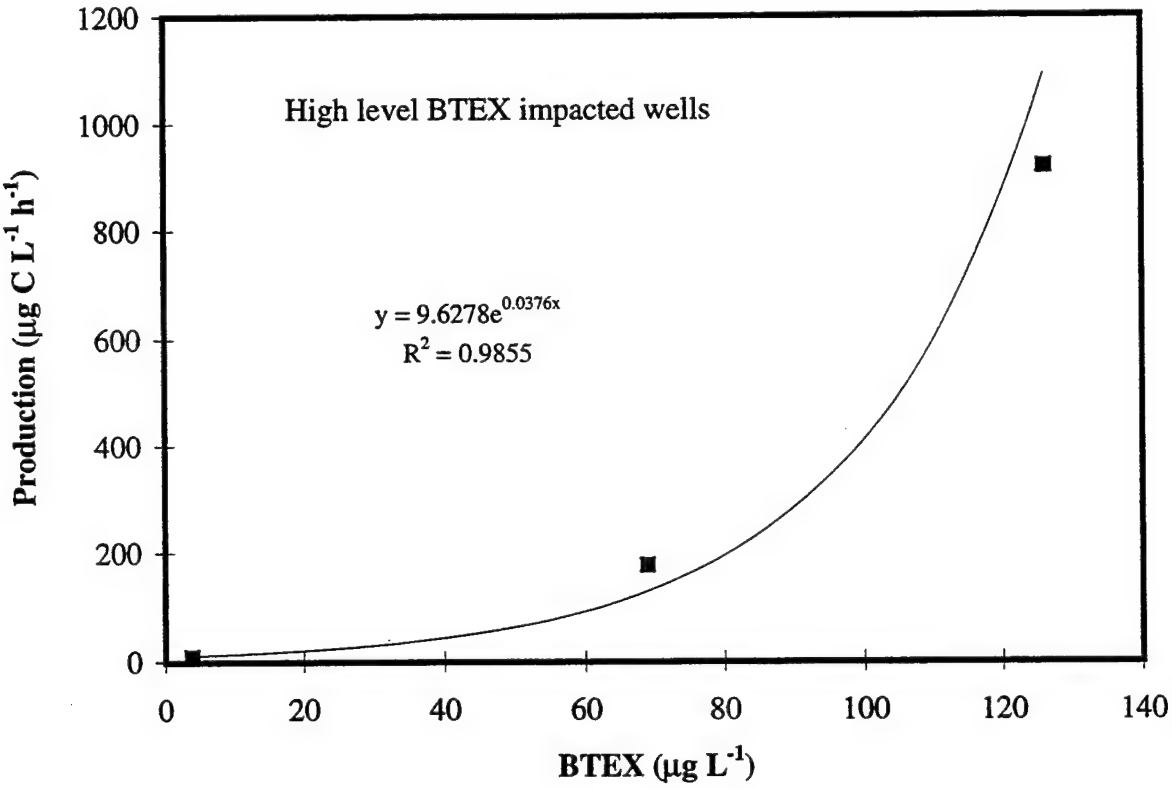

High level BTEX impacted wells
y = 9.6278e^0.0376x
R^2 = 0.9855
Production (µg C L-1 h-1)
BTEX (µg L-1)
0
200
400
600
800
1000
1200
0
20
40
60
80
100
120
140

Figure 12.

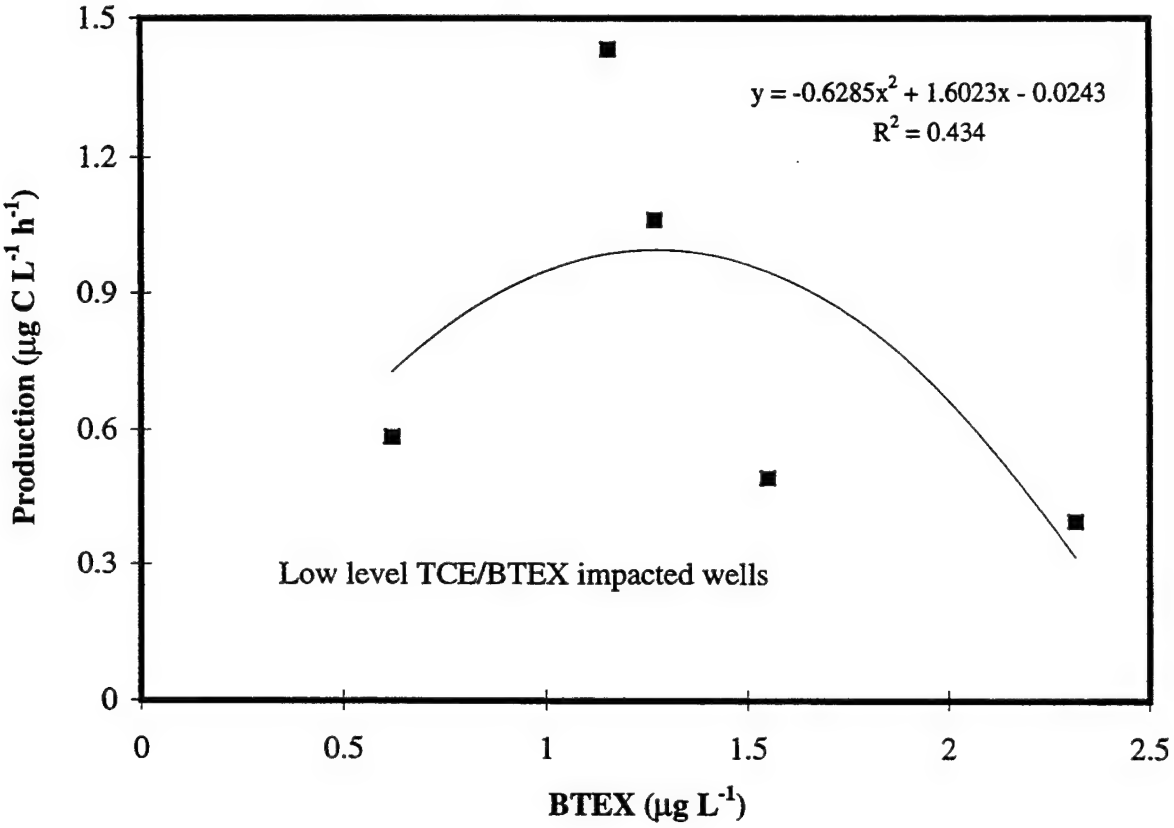

y = -0.6285x² + 1.6023x - 0.0243
R² = 0.434
Low level TCE/BTEX impacted wells
Production (µg C L⁻¹ h⁻¹)
BTEX (µg L⁻¹)
0
0.3
0.6
0.9
1.2
1.5
0
0.5
1
1.5
2
2.5

Figure 13.

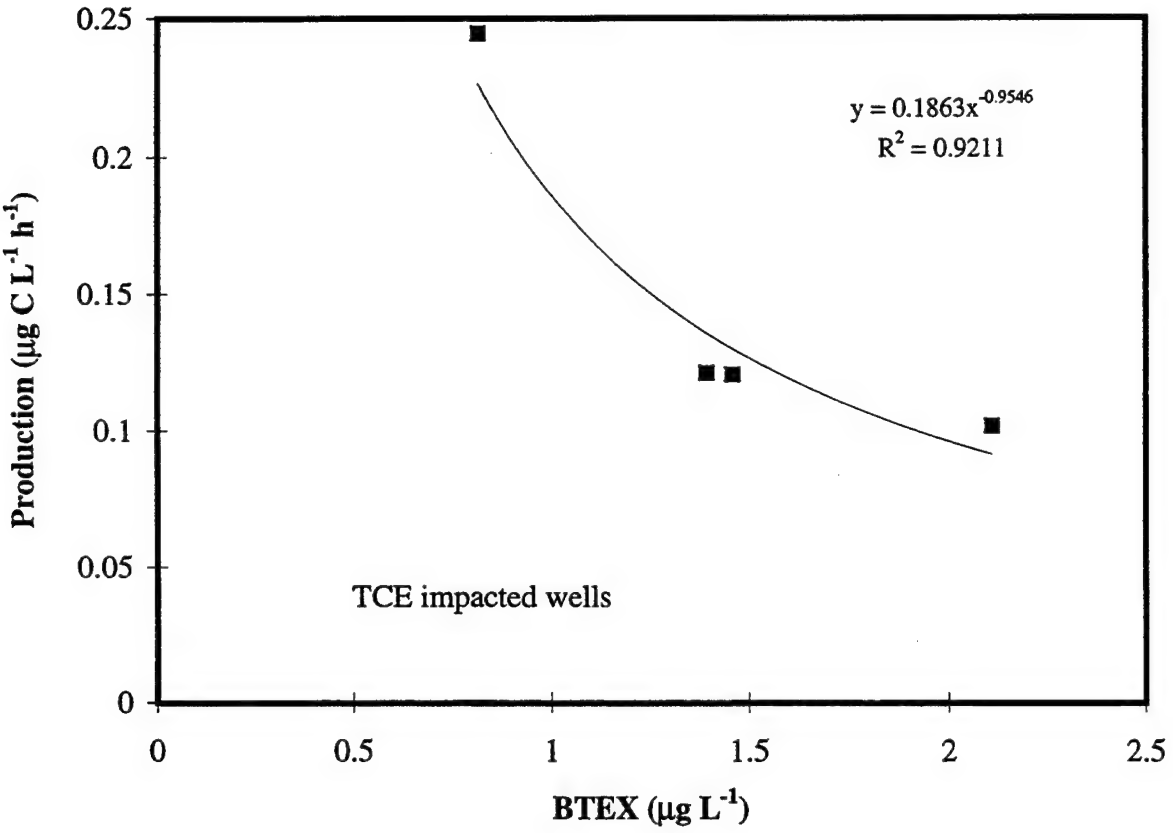

0.25
0.2
0.15
0.1
0.05
0
0
0.5
1
1.5
2
2.5
Production (µg C L-1 h-1)
BTEX (µg L-1)
y = 0.1863x-0.9546
R2 = 0.9211
TCE impacted wells

Figure 14.

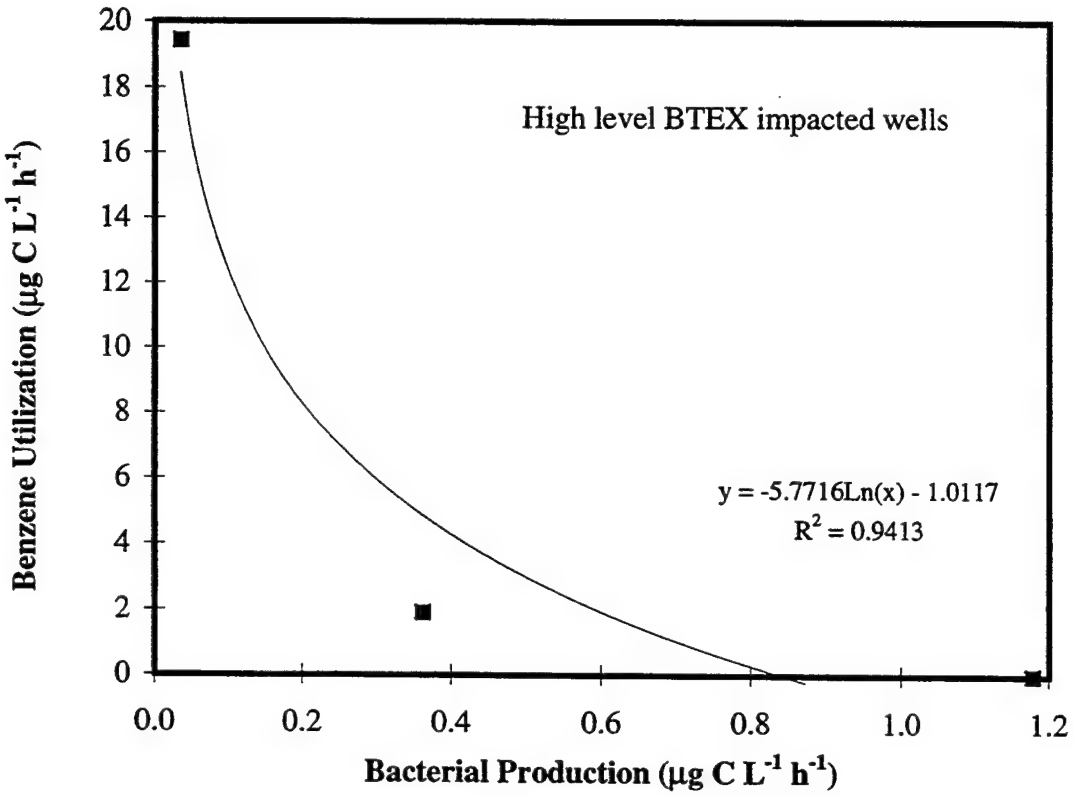

High level BTEX impacted wells
y = -5.7716Ln(x) - 1.0117
R2 = 0.9413
Benzene Utilization (µg C L-1 h-1)
Bacterial Production (µg C L-1 h-1)
0
2
4
6
8
10
12
14
16
18
20
0.0
0.2
0.4
0.6
0.8
1.0
1.2

Figure 15.

Figure 16.

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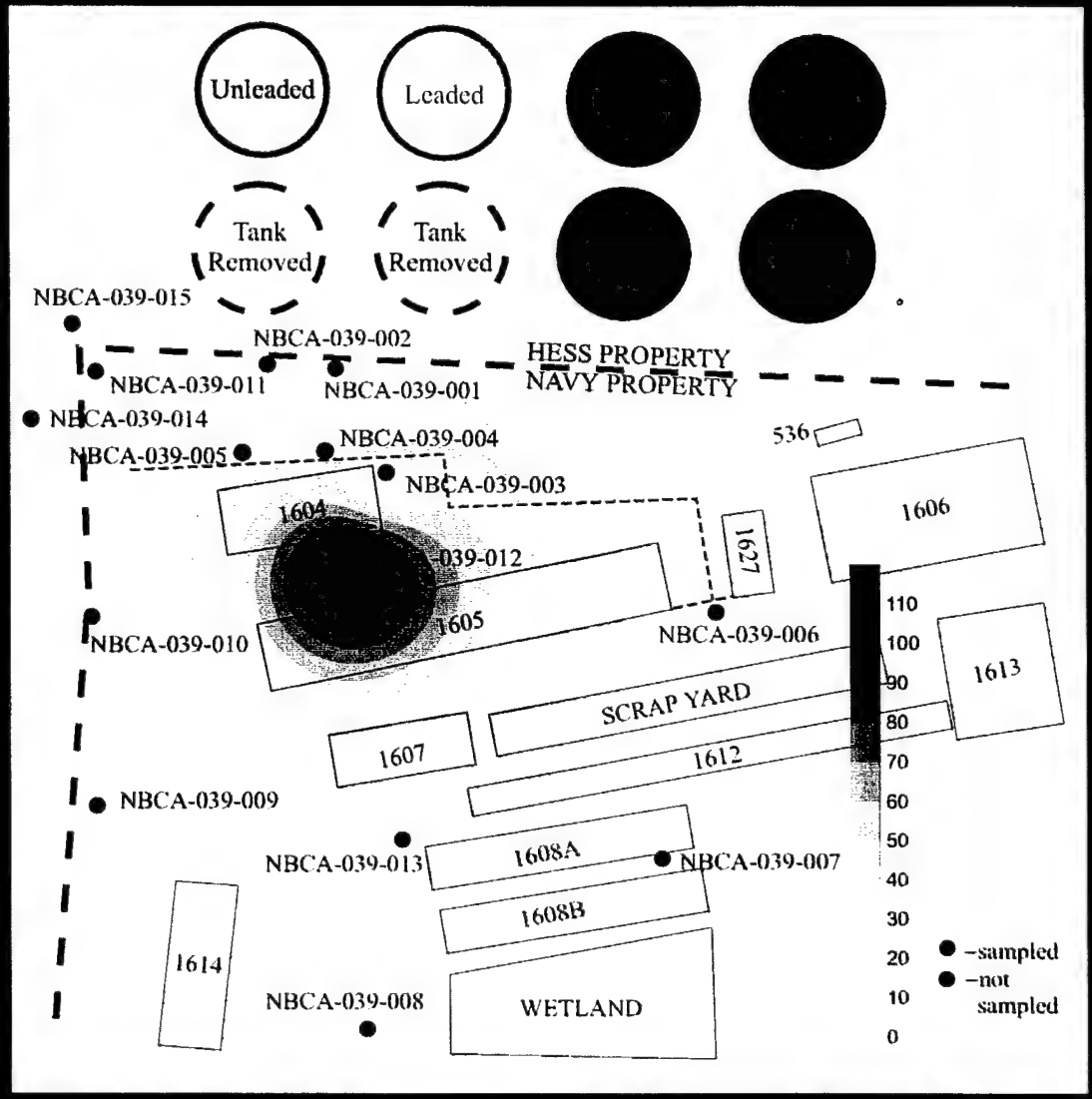
Phase I DRMO Site 21-23 July 1997

TCE concn. (relative abundance) is elevated in MW-12 with lower concn. downgradient.



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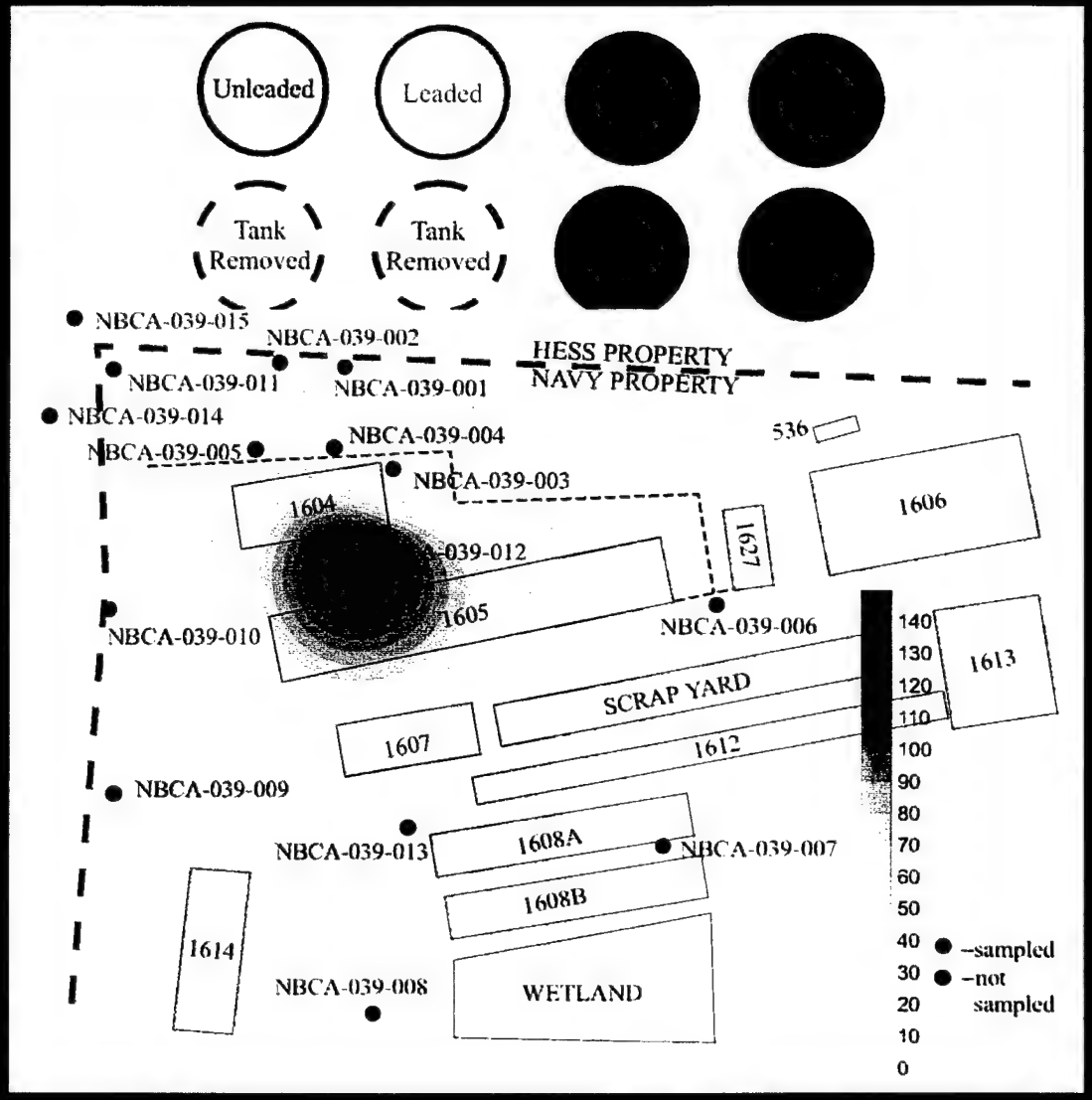

Figure 17.

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Phase I DRMO Site 21-23 July 1997

Toluene turnover times (h^{-1}) were very rapid in the TCE plume.

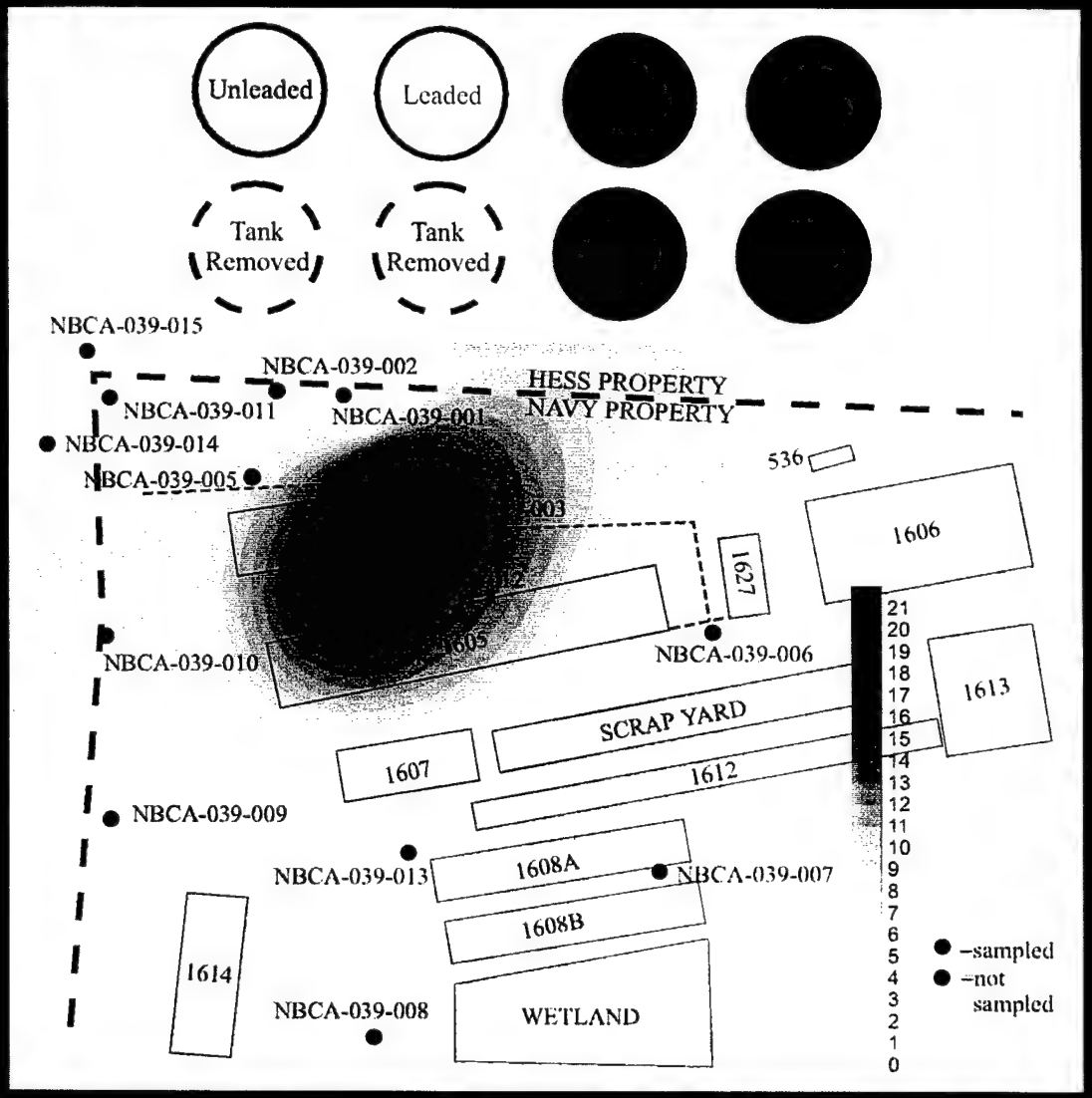

Figure 18.

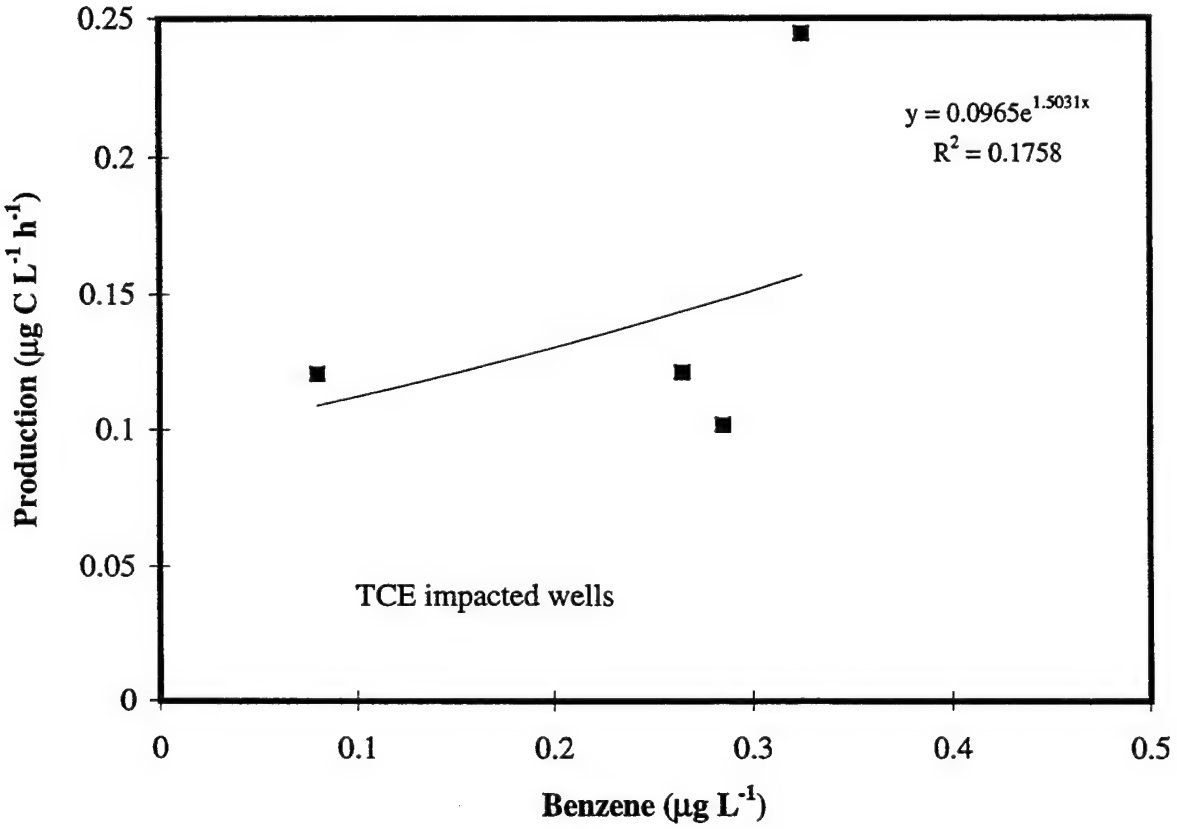
0.25
0.2
0.15
0.1
0.05
0
0
0.1
0.2
0.3
0.4
0.5
Production (µg C L-1 h-1)
Benzene (µg L-1)
y = 0.0965e1.5031x
R2 = 0.1758
TCE impacted wells

Figure 19.

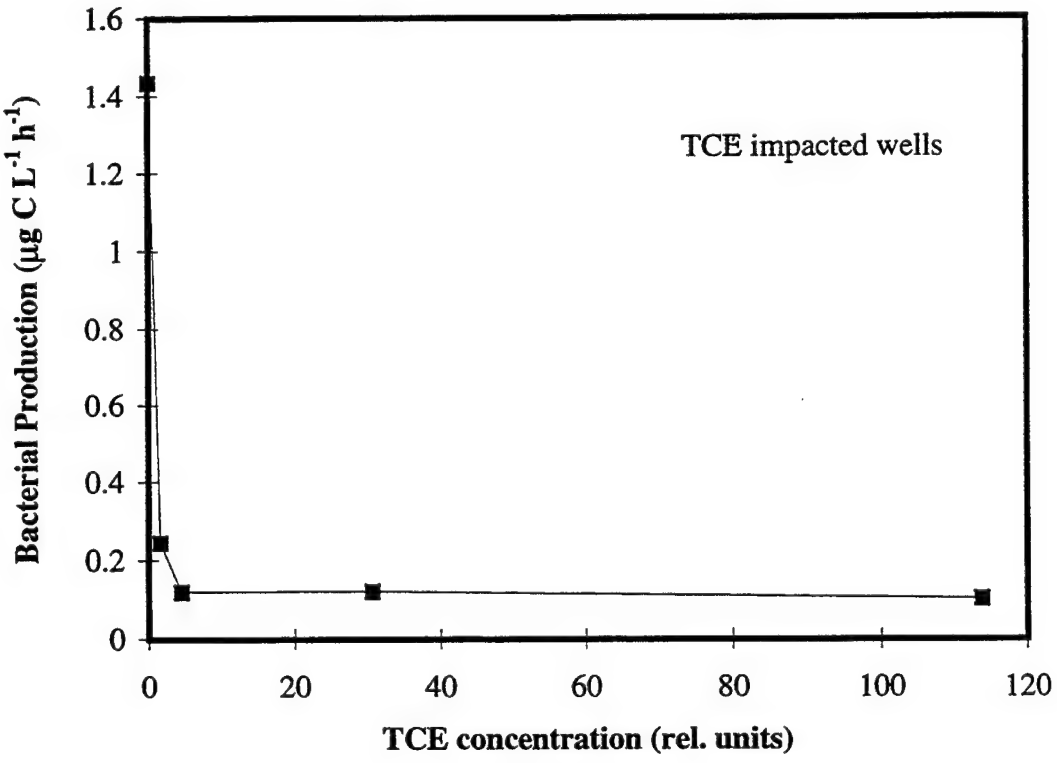
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Bacterial Production (µg C L-1 h-1)
TCE impacted wells
0
20
40
60
80
100
120
TCE concentration (rel. units)

Figure 20.

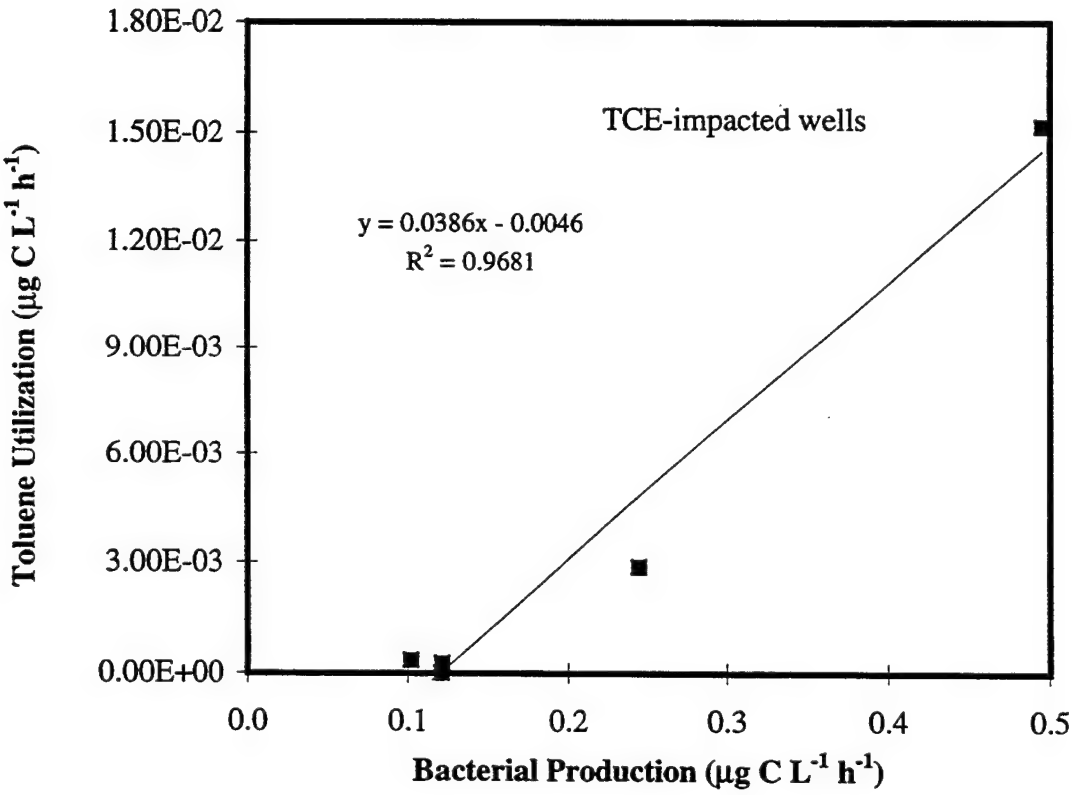
1.80E-02
1.50E-02
1.20E-02
9.00E-03
6.00E-03
3.00E-03
0.00E+00
Toluene Utilization (µg C L-1 h-1)
TCE-impacted wells
y = 0.0386x - 0.0046
R2 = 0.9681
0.0
0.1
0.2
0.3
0.4
0.5
Bacterial Production (µg C L-1 h-1)

Figure 21.

Figure 22.

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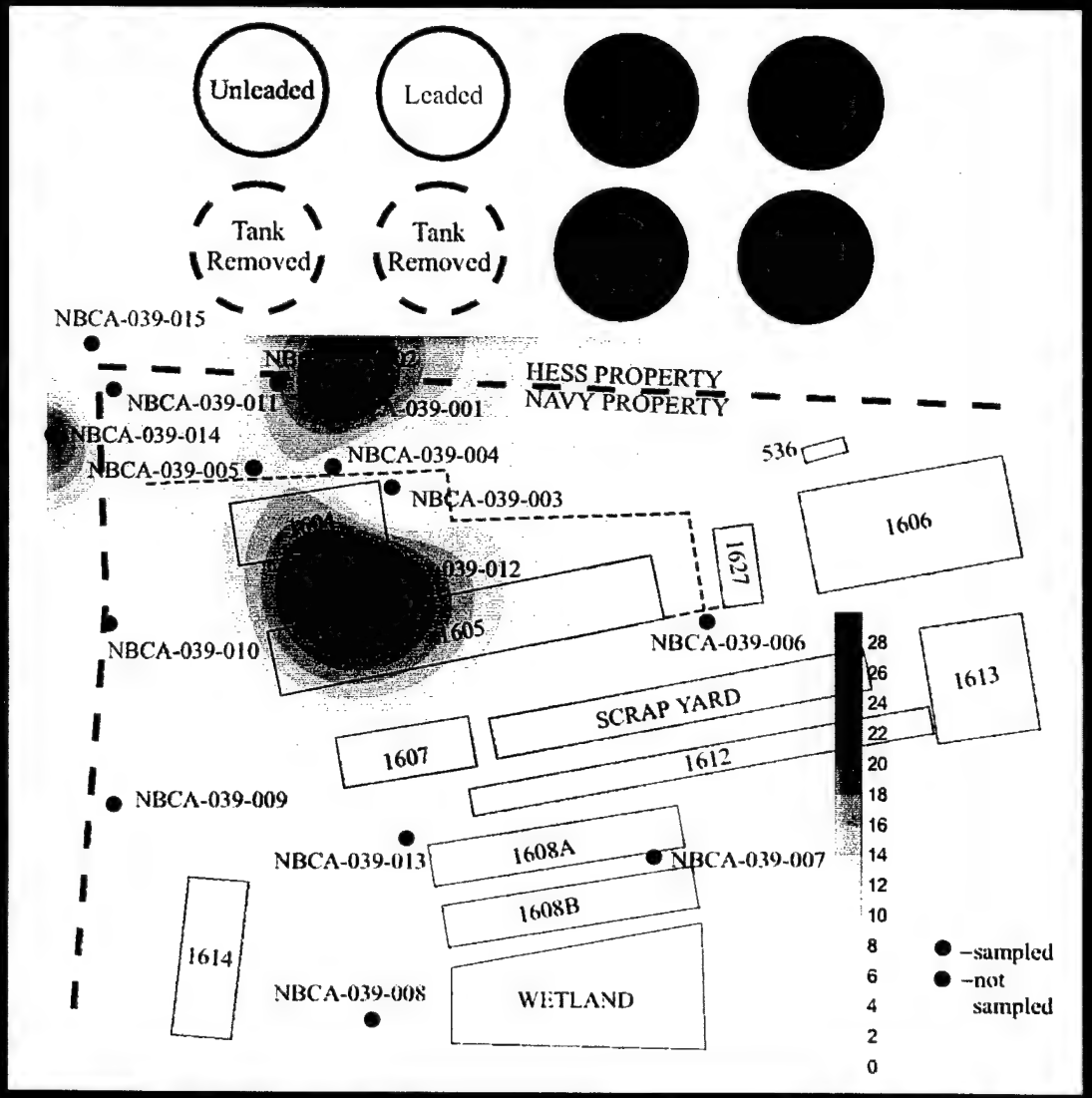
Phase I DRMO Site 21-23 July 1997

MTBE concn. ($\mu g\ l^{-1}$) is elevated in MW-1, -12, & -14 suggesting at least two sources are present.



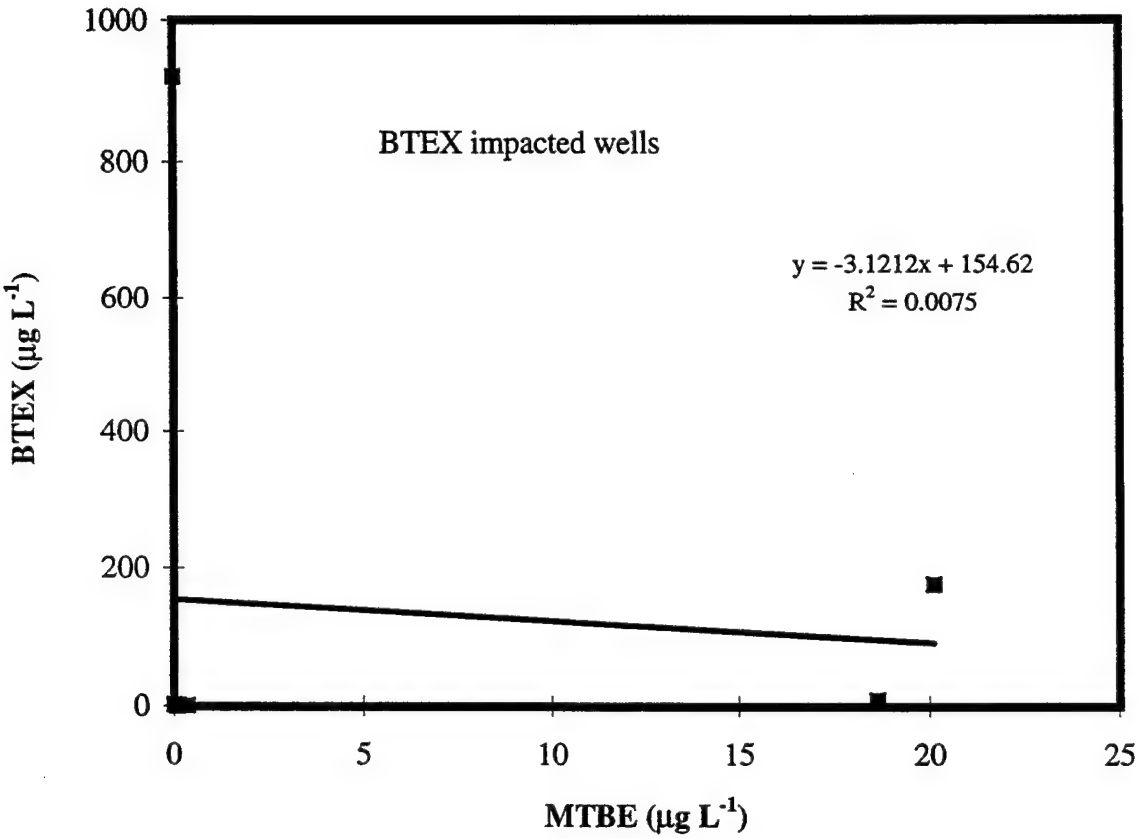

BTEX impacted wells
y = -3.1212x + 154.62
R2 = 0.0075
BTEX (µg L-1)
MTBE (µg L-1)
1000
800
600
400
200
0
0
5
10
15
20
25

Figure 23.

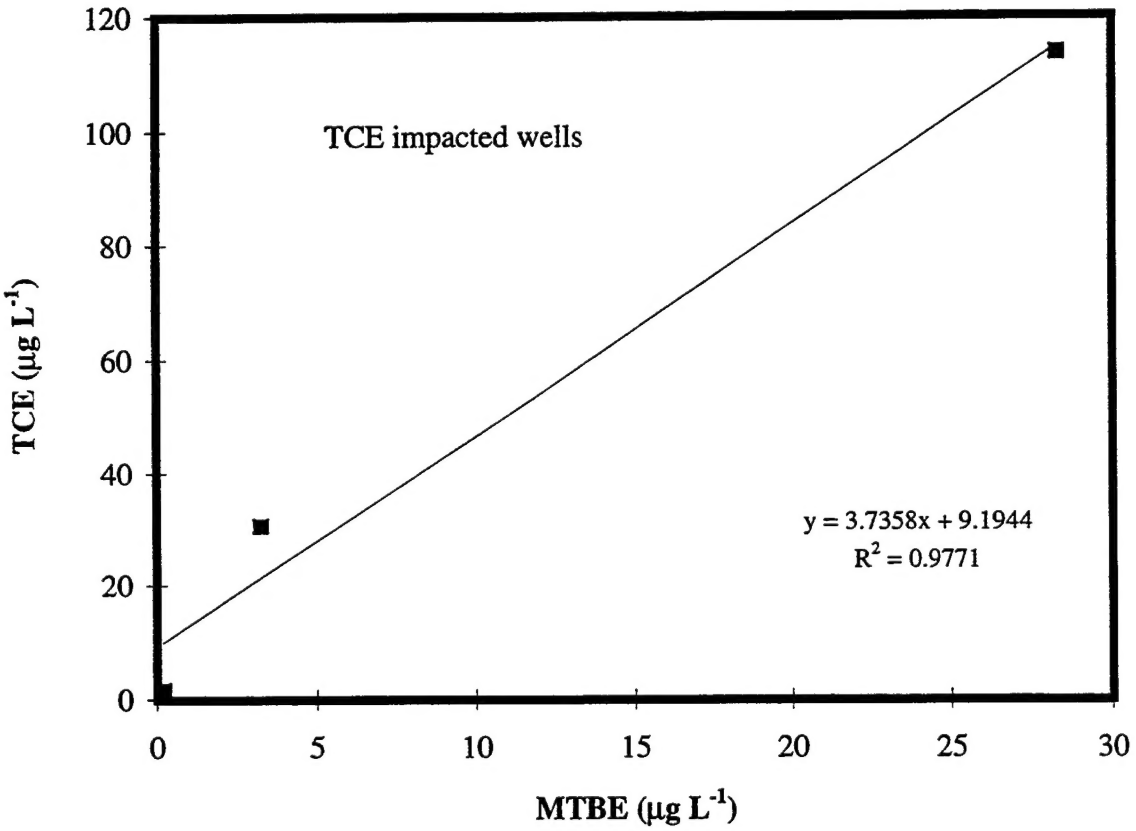

TCE impacted wells
y = 3.7358x + 9.1944
R2 = 0.9771
TCE (µg L-1)
MTBE (µg L-1)
0
20
40
60
80
100
120
0
5
10
15
20
25
30

Figure 24.

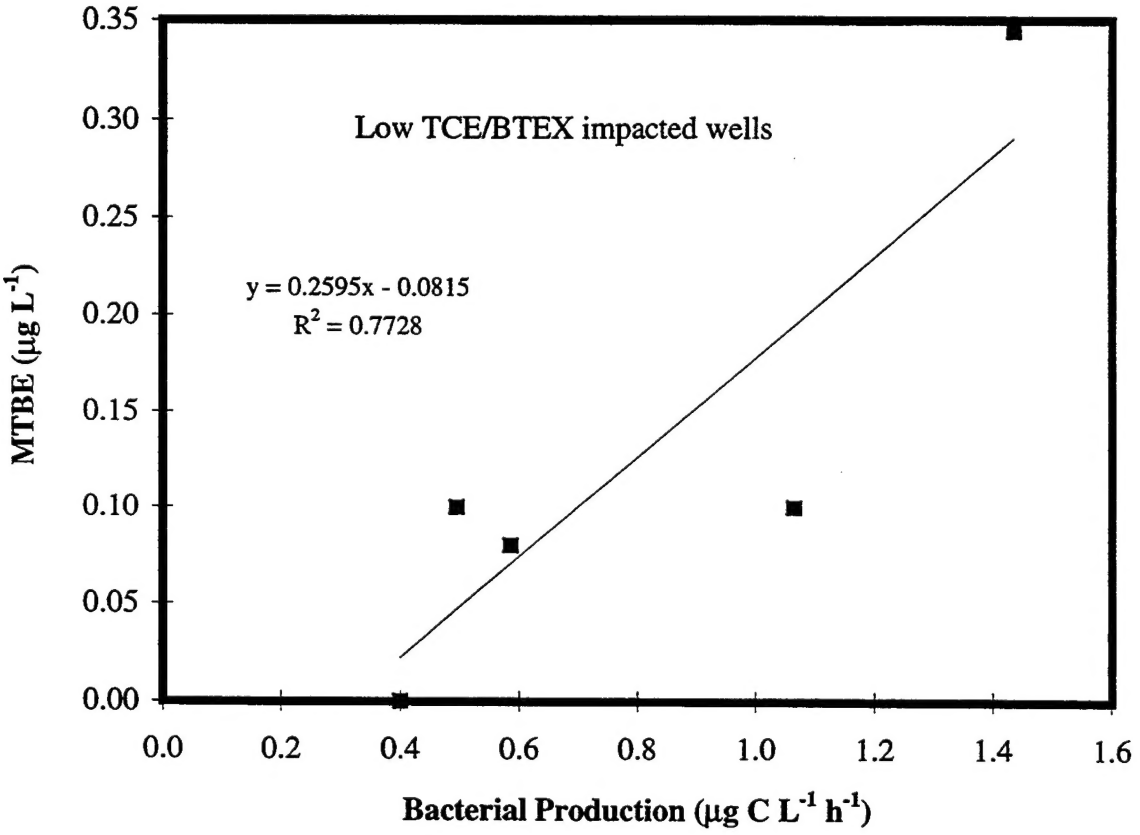

Low TCE/BTEX impacted wells
y = 0.2595x - 0.0815
R2 = 0.7728
MTBE (µg L-1)
Bacterial Production (µg C L-1 h-1)
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6

Figure 25.

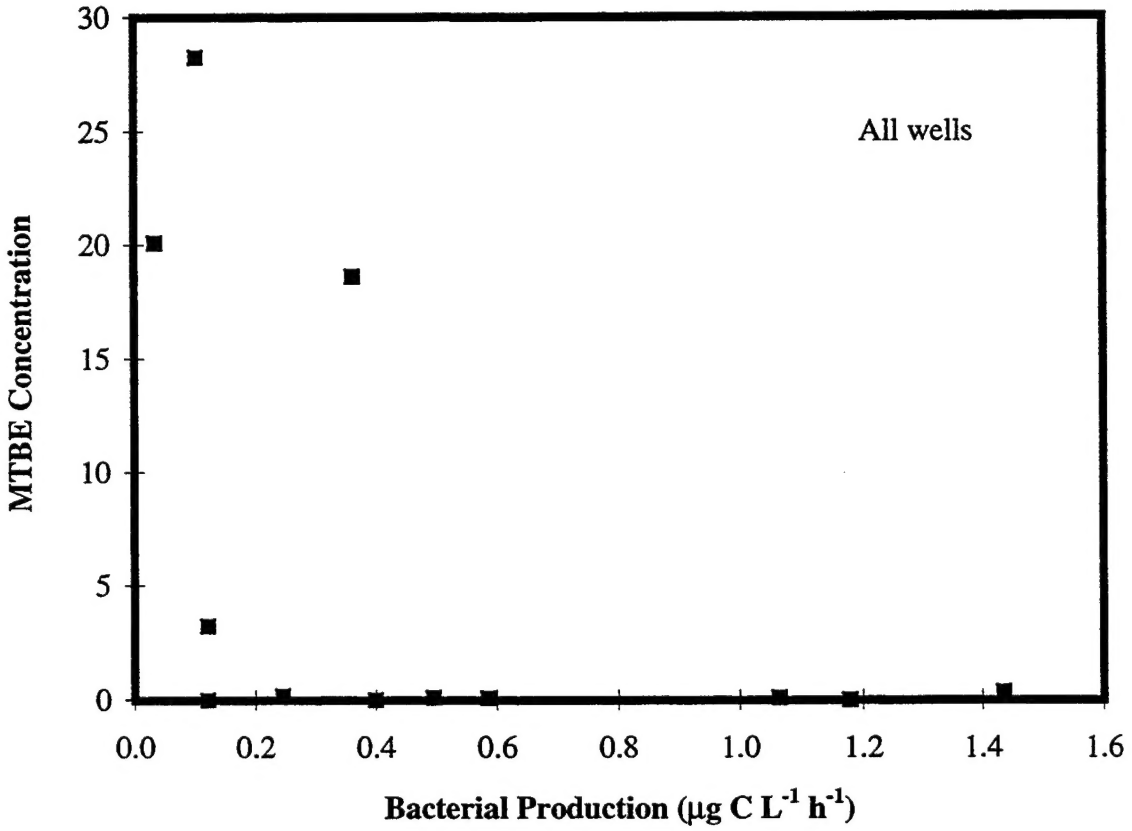

All wells
MTBE Concentration
Bacterial Production (µg C L-1 h-1)
0
5
10
15
20
25
30
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6

Figure 26.

NBCA 039-	MTBE µg L-1	Benzene µg L-1	Toluene µg L-1	Ethylbenzene µg L-1	o, m-xylene µg L-1	p-xylene µg L-1	Total BTEX µg L-1	DCE µg L-1	*TCE* µg L-1	DCE:TCE	Production µg C L-1 h-1	Benzene Utilization µg C L-1 h-1	Toluene Utilization µg C L-1 h-1
1	**20.10**	**69.00**	**1.05**	**44.92**	**59.10**	**3.13**	**177.20**	**0.00**	**0.00**	**0.00**	**3.43E-02**	**1.94E+01**	**7.33E-01**
3	*3.26*	*0.27*	*0.00*	*0.49*	*0.64*	*0.00*	*1.40*	*3.88*	*30.63*	*0.13*	*1.21E-01*	0.00E+00	1.47E-03
6	0.10	0.45	0.00	0.57	0.00	0.54	1.55	0.00	0.00	0.00	4.95E-01	3.30E-01	1.52E-02
7	0.08	0.13	0.00	0.49	0.00	0.00	0.62	0.00	0.00	0.00	5.85E-01	7.78E-02	2.61E-01
8	0.00	0.30	0.00	0.80	0.67	0.55	2.32	0.00	0.00	0.00	3.99E-01	0.00E+00	9.86E-03
9	*0.19*	*0.33*	*0.00*	*0.49*	*0.00*	*0.00*	*0.82*	*29.46*	*1.62*	*18.16*	*2.45E-01*	6.84E-02	1.59E-02
10	0.35	0.04	0.00	0.50	0.00	0.62	1.16	0.00	0.00	0.00	1.43E+00	0.00E+00	7.11E-03
11	**0.00**	**126.00**	**0.00**	**227.00**	**513.50**	**54.00**	**920.50**	**0.00**	**0.00**	**0.00**	**1.18E+00**	**0.00E+00**	**0.00E+00**
12	*28.28*	*0.29*	*0.00*	*0.62*	*0.67*	*0.54*	*2.11*	*149.02*	*113.81*	*1.31*	*1.02E-01*	1.15E-01	1.88E-03
13	*0.00*	*0.08*	*0.00*	*0.71*	*0.67*	*0.00*	*1.46*	*23.62*	*4.51*	*5.24*	*1.21E-01*	6.78E-02	0.00E+00
14	**18.63**	**3.78**	**0.00**	**2.78**	**0.00**	**3.00**	**9.55**	**0.00**	**0.00**	**0.00**	**3.62E-01**	**1.91E+00**	**0.00E+00**
15	0.10	0.13	0.00	0.61	0.00	0.53	1.27	0.00	0.00	0.00	1.06E+00	2.52E-01	3.42E-02

Relatively unimpacted wells
Wells highly impacted with TCE
Wells highly impacted with BTEX

Table 1. Contaminant concentrations and biological analyses from July 21-23, 1997 sampling of CNY DRMO site.